

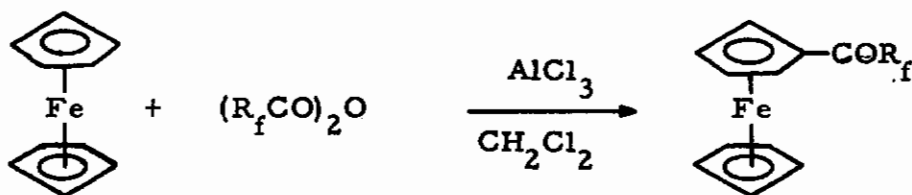
A STUDY OF THE FRIEDEL-CRAFTS ACYLATION OF FERROCENE WITH PERFLUOROCARBOXYLIC ACID DERIVATIVES

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Since the discovery of bis(cyclopentadienyl)iron or ferrocene in 1950 numerous derivatives of this unique organometallic compound have been prepared and their properties studied. In connection with a program involving the synthesis of polymeric derivatives of ferrocene, it was of interest to investigate methods for the preparation of fluorine-containing ferrocene monomers and polymers. Initially this involved the preparation and study of model compounds representative of new types of ferrocenes, such as the hitherto unknown perfluoroalkylferrocenyl ketones, 1,1-dihydroperfluoroalkylferrocenes, and perfluoroalkylferrocenes. In this paper are reported some of the preliminary results obtained in the investigation of synthetic approaches to the perfluoroalkylferrocenyl ketones, $C_5H_5Fe-C_5H_4COR_f$, as well as some observations and conclusions resulting from a study of the rather well-known Friedel-Crafts reaction with ferrocene.

Acylation of ferrocene with perfluorocarboxylic acid anhydrides was carried out to yield the desired perfluoroacylferrocenes in accordance with the following general reaction:



where $R_f = CF_3-$, C_2F_5- , and C_3F_7-

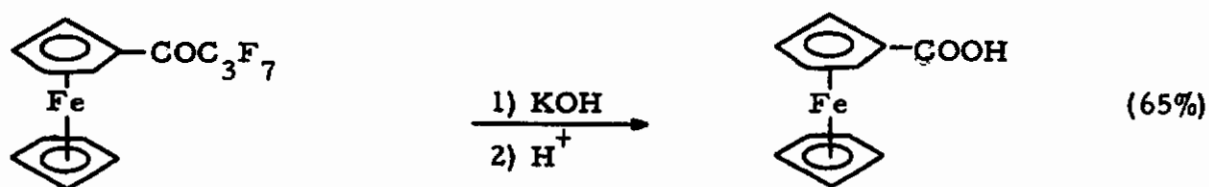
The reactions were conducted in methylene chloride using anhydrous aluminum chloride as the catalyst. In these acylations, only monosubstituted ketones were isolated (in 30-40% yield) even when conditions favoring diacylation were employed,

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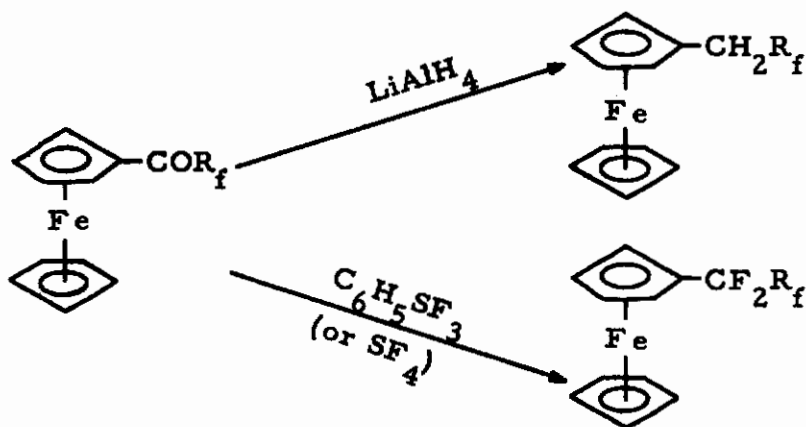
i. e., slow addition of ferrocene to the anhydride-aluminum chloride mixture.

Acylation of ferrocene involving the substitution of a perfluoroacyl halide for the anhydride, in general, gave lower yields of the ketones. The yield of perfluoropropylferrocenyl ketone from the reaction of perfluorobutyryl chloride and ferrocene was found to be less than 10%.

Solid, crystalline 2, 4-dinitrophenylhydrazones were prepared from the perfluoromethyl- and perfluoroethylferrocenyl ketones, but could not be obtained from the perfluoropropyl homolog by conventional procedures. In an attempt to prepare the oxime of the latter compound, using hydroxylamine hydrochloride and excess potassium hydroxide in absolute ethanol, ferrocenemonocarboxylic acid was obtained upon acidification of the reaction mixture.

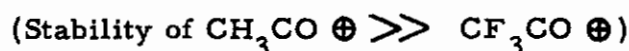


Reduction of the ketones to 1, 1-dihydroparfluoroalkylferrocenes and conversion of the ketones to perfluoroalkylferrocenes is presently under investigation according to the following general reactions:



where $\text{R}_f = \text{CF}_3^-$, C_2F_5^- , and C_3F_7^-

Acylation of ferrocene using non-fluorine-containing acyl compounds, such as acetyl chloride, are known to occur in good yields (1) and, in many cases, with additional formation of diacylferrocenes. The electron-withdrawing nature of a perfluoroalkyl group adjacent to the carbonyl carbon of the perfluoroacyl derivative gives rise to acylium intermediates of very limited stability. On the other hand, methyl (or alkyl) groups on the carbonyl carbon tend to stabilize acylium ions.



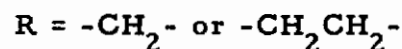
Consequently, perfluoro acid derivatives are far less reactive in Friedel-Crafts acylations than their aliphatic analogs.

Moreover, the apparent absence of bis(perfluoroacyl)ferrocenes is probably a result of the large electron-withdrawing and deactivating effect of a perfluoroacyl group attached to the ferrocene nucleus.

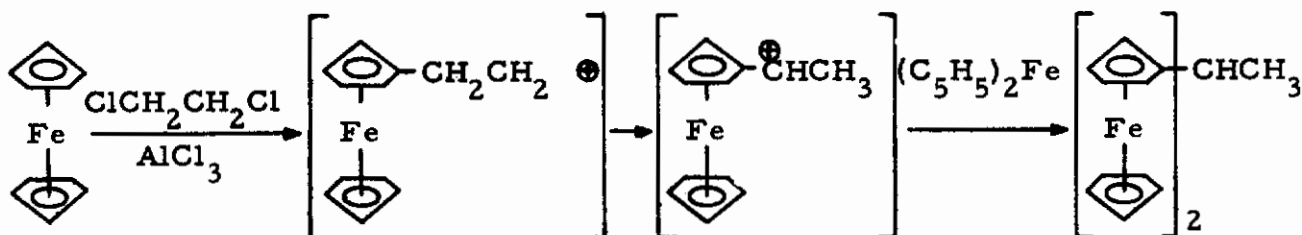
The sluggish reactivity of perfluoroacyl compounds in the above reactions most likely enables a considerable quantity of unacylated ferrocene to enter into concomitant reactions, possibly with the solvent or aluminum chloride. This is evidenced by the repeated isolation of non-fluorine-containing brown powders and resins as by-products.

Nesmeyanov et. al. (2, 3) have studied the reactions of ferrocene and methylene and ethylene chloride in the presence of anhydrous aluminum chloride. When these reactions were carried out at or near the boiling point of the solvent involved, "polyalkanodiferrocenes" were reported as the products of the reaction.

Structure of
pentaalkanodiferrocenes
(Nesmeyanov)

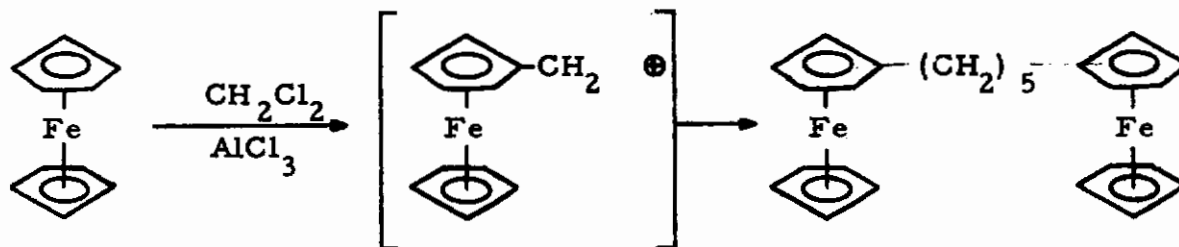


By using different mole ratios of ferrocene to ethylene chloride a diferrocenylethane was isolated (4). Rinehart (5) proved that this compound was actually 1,1-diferrocenylethane whose formation presumably resulted from a carbonium ion rearrangement which occurred during the course of the reaction.

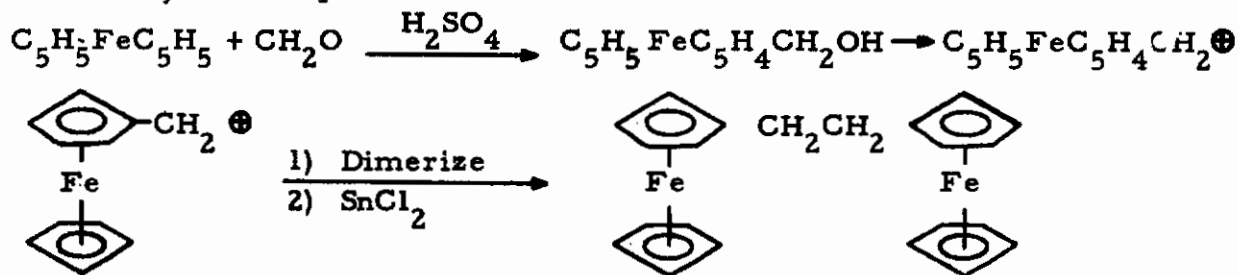


In view of this evidence it does not seem likely that 1,2-ethane bridges would be formed in "pentaethanodiferrocene." However, the absence of methyl groups was indicated on examination of the infrared spectrum of the pentaethano compound which would disprove the presence of any CH_3CH -linkages.

With pentamethanodiferrocene, the formation of a methylene bridge in the presence of aluminum chloride would be expected to occur via the carbonium on:



However, evidence has been presented (6) which shows that this unique carbonium species (from formaldehyde and ferrocene in sulfuric acid) combines to give 1,2-diferrocenylethane upon reduction:



The present authors have studied the reaction of methylene chloride and ethylene chloride with ferrocene in the presence of aluminum chloride at room temperature or lower (in ferrocene/aluminum chloride mole ratios of 2:3).

With methylene chloride no reaction other than oxidation to ferrocinium ion occurred at temperatures of -30° or lower when the reaction mixture was hydrolyzed after 5 hours of stirring at the low temperature. However, if, after the 5 hours of stirring at the low temperature, the reaction mixture was allowed to warm to room temperature and then stirred at this temperature for an additional 18 hours, five distinct products were isolated. The separation of these products was based primarily on differences in solubilities of the materials in different solvents. These products and some of their properties are listed in Table I. With the exception of the formation of compound V, ethylene chloride with ferrocene and aluminum chloride gave the same products as when methylene chloride was used as the solvent, both by the procedure of Nesmeyanov *et. al.* (4) or by a procedure similiar to the above methylene chloride reaction.

TABLE I

COMPOUND	M. P.	COLOR	YIELD*	SOLUBILITY
I	78-80 $^{\circ}$	yellow	0.34g	moderately sol. in methanol
II**	138-139	yellow	0.2 g	sol. in ether, ppt. with MeOH, sol. in cyclohexane
III	178-180	yellow	3.2 g	insol. in ether, sol. in benzene, ppt. with MeOH, sol. in cyclohexane
IV	dec. > 250 $^{\circ}$	brown	1 g	insol. in cyclohexane, sol. in benzene
V	dec. 180 $^{\circ}$	yellow	0.3 g	slightly sol. in pet. ether, b.p. 30-60 $^{\circ}$; Recryst. from methanol

*Based on the use of 37.2g of ferrocene and 40g of AlCl_3 . The yield is based on purified material.

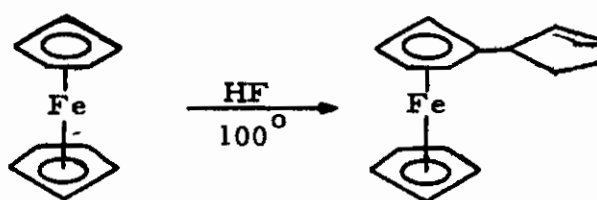
****Pentaethanodiferrocene**

The separation of the materials was difficult and often required many repeated extractions. All compounds had bands in the 9-10 region of their infrared spectra. According to the separation procedure described by Nesmeyanov et. al. (4), compound II is apparently "pentaethanodiferrocene." Compound I has an infrared spectrum almost identical to that of compound III and perhaps is a lower molecular weight precursor of the latter. Compound I was originally obtained as a resinous material from a cyclohexane elution of a sample placed on an alumina column in petroleum ether (b. p. 30-60°). It was later found that a better method of purification of this compound may be effected based on its partial solubility in methanol from which it can be obtained in the form of a yellow powder, m. p. 78-80°.

Compound II (presumably pentaethanodiferrocene) is distinguished easily from the other products because in its infrared spectrum it contains a band in the 7.9u (1260cm) region which is extremely intense when the compound is pure.

The fact that all of these compounds (except V) have been isolated from either methylene chloride or ethylene chloride indicated that the reaction products were formed independent of the chemical nature of the solvent employed. This led to the question of how aluminum chloride might affect ferrocene in the presence of polar solvents but in the absence of strong alkylating agents, acylating agents, or other electrophiles.

Anhydrous hydrogen fluoride (a moderately strong Lewis acid) has been reported to catalyze the acetylation of ferrocene. However, when no acylating agent was present, anhydrous hydrogen fluoride cleaved some of the ferrocene (at 100°) and cyclopentenylferrocene was obtained as the product.



The present authors have found that shaking ferrocene and trifluoroacetic anhydride in HF for two days at room temperature did not result in acylation of the ferrocene but in the formation of cyclopentenylferrocene.

It is believed that excess aluminum chloride also causes a similar cleavage-acylation reaction in the absence of strong acylating or alkylating agents. In this connection it may be noted that the analysis of "pentaethanodiferrocene" reported by Nesmeyanov et. al. (2) is in close agreement with the calculated percentage composition of cyclopentenylferrocene (dimer) as shown in Table II.

TABLE II

ANALYTICAL DATA ON PENTAETHANODIFERROCENE			
Element	Found for (2) Pentaethanodiferrocene %	Calculated for (2) Pentaethanodiferrocene %	Calculated for Cyclopentenylferrocene %
C	71.64, 71.50	71.74	71.46
H	6.25, 6.30	6.02	6.34
Fe	21.70, 22.25	21.90	22.2

One difference between hydrogen fluoride and aluminum chloride is the greater strength of the latter as a Lewis acid. Thus it would be expected that aluminum chloride would favor further alkylation of ferrocene by "cyclopentadienyl fragments" or the formation of polymeric materials. (Hydrogen fluoride gives monomeric, aluminum chloride gives polymeric materials.)

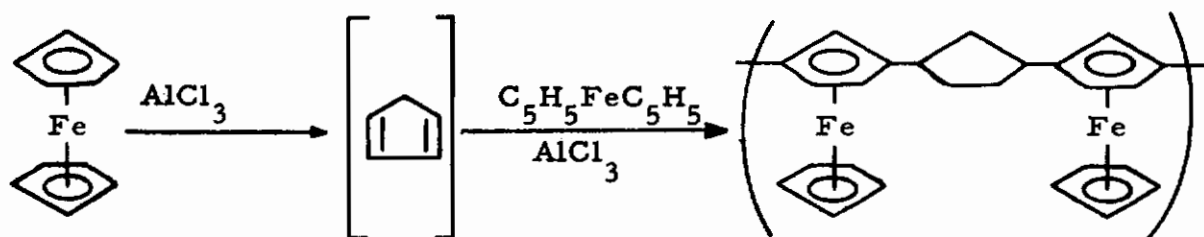
It was initially believed that in the aluminum chloride-alkylene chloride-ferrocene

reactions, cyclopentenyl ferrocene may be an intermediate in the formation of dimeric and polymeric materials made up of ferrocene and cyclopentyl residues. However, preliminary experiments in which cyclopentenyl ferrocene was treated with aluminum chloride in methylene chloride, led to recovery of most of the ferrocene starting material. There was evidence that only a trace of compound II was formed (when the reaction was carried out at room temperature for 18 hours.) Weinmayr (7) also pointed out that cyclopentenyl ferrocene did not react with benzene in the presence of hydrogen fluoride. However, when benzene, ferrocene and anhydrous hydrogen fluoride were reacted together a phenylcyclopentylferrocene was obtained.

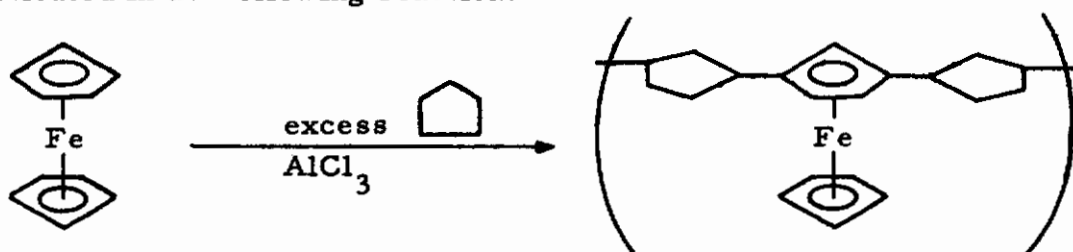


This indicated that phenylcyclopentylferrocene is not formed through a cyclopentenyl intermediate. Such evidence points to the fact that perhaps the important intermediate in all of these reactions is the "cyclopentadienyl fragment" which arises from the cleavage of ferrocene with hydrogen fluoride or aluminum chloride.

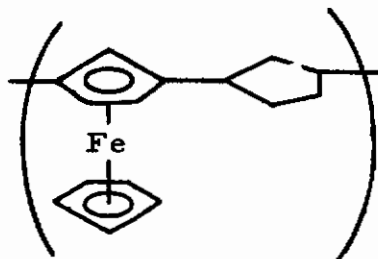
The mole ratio of aluminum chloride to ferrocene, the temperature and the relative polarity of the solvent may play a role in determining the nature of the products isolated in the reaction of ferrocene, alkylene halides and aluminum chloride. The experiment of Nesmeyanov et. al., using smaller quantities of aluminum chloride (at one time) in methylene chloride and higher temperatures, favored products possibly arising from the following reaction:



However, at lower temperatures and with higher concentrations of aluminum chloride, the ratio of cleavage products of ferrocene to unreacted ferrocene was favored. This, in turn, has apparently led to the formation of products of the type indicated in the following reaction:



Conditions intermediate to the above two cases may have led to compounds possessing the following structures:

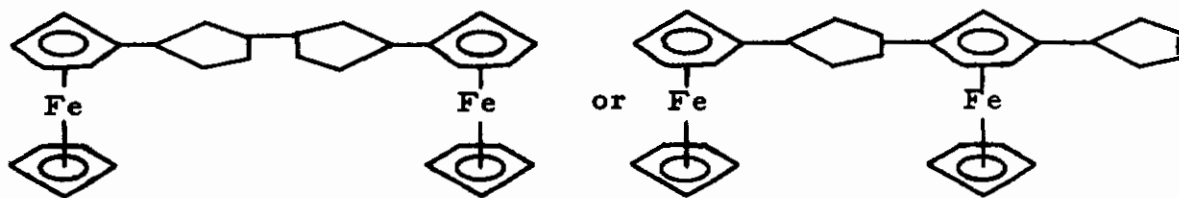


The analytical data seems to point out the fact that the materials isolated in the ferrocene-aluminum chloride-alkylene chloride reactions are made up of combinations of ferrocene and "five methylene groups" (or cyclopentyl groups.)

The available elemental analysis and molecular weight data on compounds I-V and the structures proposed for these compounds are summarized below.

1. Compound I, m. p. 78-80°

Proposed structures:



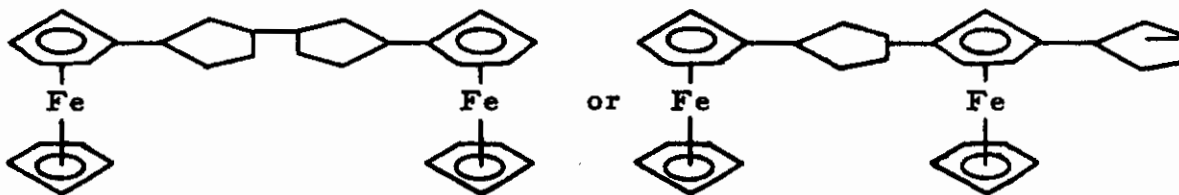
Calc. for $C_{30}H_{32}Fe_2$: C, 71.46%; H, 6.34%; Fe, 22.2%

M. W. 504

Found: C, 71.24%; H, 6.36%; Fe, 24.2%*
71.00%; H, 6.23%; Fe, 24.4%*

* The iron is suspected as being high and is being repeated. M. W. not received

2. Compound II ("pentaethanodiferrocene"), m. p. 138-139°



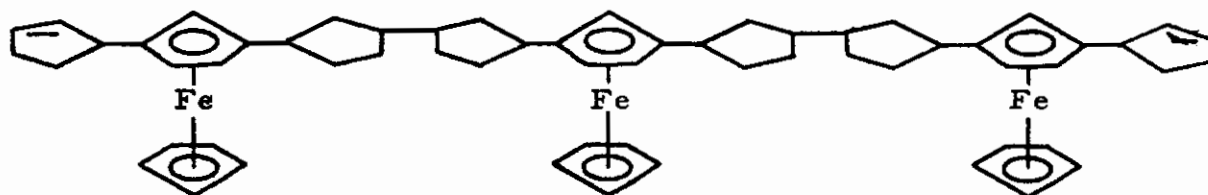
Calc. for $C_{30}H_{32}Fe_2$: C, 71.46; H, 6.34; Fe, 22.2%

M. W. 504

Found: C, 71.64; H, 6.25; Fe, 21.70
C, 71.50; H, 6.30; Fe, 21.90

M. W. 545, 568

3. Compound III, m. p. 178-180°



Calc. for $C_{60}H_{70}Fe_3$: C, 75.17; H, 7.35; Fe, 17.47

M. W. 958

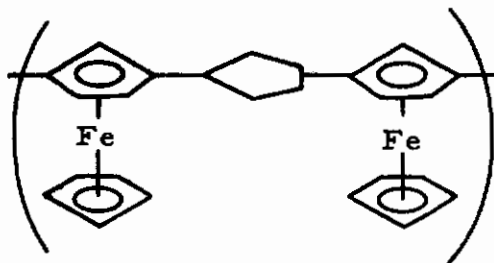
Found: C, 76.37; H, 6.89; Fe, 16.50
C, 76.39; H, 6.87; Fe, 16.83

M. W. ca. 1000

4. Compound IV.

The analysis had not been received at the time this paper was prepared. Its infrared spectrum, however, is very similar to those of Compounds I and III. From its physical properties it appears to be one of the higher molecular-weight materials reported by Nesmeyanov (2).

5. Compound V.



Calc. for $C_{22}H_{20}Fe_2$: C, 66.70%; H, 5.09%

Found: C, 67.08%; H, 5.20%
C, 67.01%; H, 5.21%

This material appears to be similar to the material isolated by Nesmeyanov et. al. (3) in the reaction of ferrocene, methylene chloride, and aluminum chloride at 40°. The latter workers state that according to their analytical data their reaction products contain 2 ferrocene units per "5 methylene" fragments. The molecular weights of two materials were reported by the Russian workers as 1000 and 2000, respectively.

On the basis of the results reported in the present work, these authors believe that in products of the ferrocene-alkylene halide-aluminum chloride reactions the "five methylene groups" described by Nesmeyanov et. al. are, in reality, a cyclopentyl group and that the "pentaethano" linkage is essentially two cyclopentyl rings, joined together or separated alternately by ferrocene.

Physico-chemical studies on these materials are now under investigation. Further work on the elucidation of the structure of these materials is also planned, along with continued studies of the preparation of the fluorine-containing compounds described at the beginning of this report.

BIBLIOGRAPHY

1. R. B. Woodward, M. Rosenblum, and M. C. Whiting, J. Am. Chem. Soc., 74, 3458 (1952); V. Weinmayr, J. Am. Chem. Soc., 77, 3009 (1955); A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, and O. A. Nesmeyanova, Doklady Akad. Nauk SSSR, 97, 459 (1954); M. D. Rausch, M. Vogel, and H. Rosenberg, J. Org. Chem. 22, 1016 (1957).
2. A. N. Nesmeyanov and N. S. Kochetkova, Doklady Akad. Nauk. SSSR, 126, 307 (1959).
3. A. N. Nesmeyanov, U. U. Korshak, V. V. Voevodskii, N. S. Kochetkova, S. L. Sosin, R. B. Materikova, T. N. Bolotnikova, U. M. Chibrikin and N. M. Bazhin, Doklady Akad. Nauk SSSR, 137, 1370 (1961)
4. A. N. Nesmeyanov and N. S. Kochetkova, Doklady Akad. Nauk SSSR, 109, 543 (1953)
5. K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, J. Am. Chem. Soc., 82, 2082 (1960).
6. K. L. Rinehart, Jr., D. J. Michejda and P. A. Kittle, J. Am. Chem. Soc., 81, 2162 (1959).
7. V. Weinmayr, J. Am. Chem. Soc., 77, 3009 (1955).

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